Journal of Power Sources 218 (2012) 307–312

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Nanostructured Gd–CeO_2 electrolyte for solid oxide fuel cell by aqueous tape casting

A. Akbari-Fakhrabadi [a,*], R.V. Mangalaraja [a,*], Felipe A. Sanhueza [a], Ricardo E. Avila [b], S. Ananthakumar [c], S.H. Chan [d]

[a] Advanced Ceramics and Nanotechnology Laboratory, Department of Materials Engineering, University of Concepcion, Concepcion, Chile
[b] Personal Dosimetry Section, Chilean Commission of Nuclear Energy, Santiago, Chile
[c] Materials and Mineral Division, National Institute for Interdisciplinary Science and Technology, CSIR, Trivandrum 695019, Kerala, India
[d] Energy Research Institute, School of Mechanical and Aerospace Engineering, Nanyang Technological University, Singapore

HIGHLIGHTS

► Fabrication of GDC electroyte for SOFC by tape casting.
► Optimization of electrolyte slurry formulation.
► Reproducibility of green scrap tapes.
► Densification by novel flash sintering technique.

ARTICLE INFO

Article history:
Received 19 March 2012
Received in revised form
29 June 2012
Accepted 1 July 2012
Available online 7 July 2012

Keywords:
Aqueous tape casting
GDC
Electrolyte
SOFC
Flash sintering

ABSTRACT

Gadolinia-doped ceria ($Ce_{0.9}Gd_{0.1}O_{1.95}$, GDC) electrolyte was fabricated by aqueous-based tape casting method for solid oxide fuel cells (SOFCs). The ceramic powder prepared by combustion synthesis was used with poly acrylic acid (PAA), poly vinyl alcohol (PVA), poly ethylene glycol (PEG), Octanol, 2,4,7,9-tetramethyl-5-decyne-4,7-diol ethoxylate and double distilled water as dispersant, binder, plasticizer, defoamer, surfactant and solvent respectively, to prepare stable GDC slurry. The conditions for preparing stable GDC slurries were studied and optimized by sedimentation, zeta potential and viscosity measurements. Green tapes with smooth surface, flexibility, thickness in the range of 0.35–0.4 mm and 45% relative green density were prepared. Conventional and flash sintering techniques were used and compared for densification which demonstrated the possibility of surpassing sintering at high temperatures and retarding related grain growth.

1. Introduction

Nanostructured materials with enhanced desired characteristics have attracted great attention for many niche applications in recent years. The nanostructured ceramics with improved ionic conductivity have recently become one of the popular fields of research since they can be used in emerging energy conversion devices such as SOFCs [1].

SOFCs have gained widespread attention due to their high-energy conversion efficiency and low pollution. However, high temperature operation would incur materials selection issues; expensive balance of plant (BoP) and fabrication cost are the barriers towards the commercialization of SOFC. Therefore, lowering the operating temperature of SOFCs and developing the low-cost and environmentally friendly fabrication techniques are the focus of recent studies [2].

High-ionic conducting solid oxide electrolytes based on rare earth doped ceria have been intensively investigated [3]. In order to reduce the operation temperature from 1000 °C to lower temperatures, gadolinium doped ceria (GDC) solid solution formed by replacing the Ce^{4+} sites of the CeO_2 lattice by Gd^{3+} cations, has been considered as a candidate solid electrolyte material for intermediate and low temperature SOFCs [4,5].

In the case of electrolyte-supported cells, the fabrication of the electrolyte is dominated by tape casting which is a well established and cost-effective method in the electroceramics industry and is scalable for mass production [6]. Tape casting often uses a slurry containing ceramic powder, solvent, binder, plasticizer, and additives

* Corresponding authors. Tel.: +56 41 2207389; fax: +56 41 2203391.
E-mail addresses: aliakbarif@udec.cl (A. Akbari-Fakhrabadi), mangal@udec.cl (R.V. Mangalaraja).

0378-7753/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jpowsour.2012.07.005

such as de-foamer, surfactant and dispersant [7]. Traditionally, tape casting was done using organic solvents. Due to environmental, health, safety and economic reasons, aqueous-based tape casting method using water as solvent is adopted to replace the traditional organic-based tape casting method [5]. Despite these advantages, several critical challenges should be overcome which include slow drying rate of the tape, high crack sensitivity, flocculation and poor wetting of the slip due to the high surface tension of water [8,9]. Therefore, one of the main challenges in aqueous tape casting is to formulate a suitable suspension composition to avoid the defects which may occur during the drying process.

Ceramic powder as main constituent of slurry plays an important role in suspension composition. Colloidally stable nano-sized powder suspensions are known to have a markedly lower volume loading compared to suspensions with larger particle sizes [10]. There are a wide variety of processes for the synthesis of ceramic powders, which provide different properties such as particle size, shape, surface area and morphology. For particles in the nanometres range, adhering layer becomes significant and the maximum volume loading for a stable suspension is decisively lower. As a consequence of this, the green bodies resulting from nano powders usually have low green densities and are difficult to sinter to dense ceramics [11,12].

A number of sintering methods rely on the assistance of applied electric field, such as microwave sintering, electric discharge compaction (EDC), and spark plasma sintering have been used for superfast densification of ceramic powders despite each of these techniques has some limitations [13–15]. Recently, flash sintering emerged as a potential technique for fast sintering is under exploration. This is achieved by a sudden sintering event when the sample reaches a certain temperature under a given applied electrical field, thus enhancing the sintering rate and retarding grain growth [16–20].

Besides organic-based tape casting of commercially produced $Ce_{0.1}Gd_{0.9}O_{1.95}$ powder [21,22], aqueous-based tape casting of $Ce_{0.8}Gd_{0.2}O_{1.9}$ synthesized by a co-precipitation method [23] and commercially produced $Ce_{0.1}Gd_{0.9}O_{1.95}$ powder [5] have been reported.

We have earlier reported the combustion synthesis of rare earth doped ceria nano powders [24,25]. In this investigation, aqueous-based tape casting of $Ce_{0.1}Gd_{0.9}O_{1.95}$ powder prepared by combustion synthesis was used for fabricating the SOFC electrolyte. The characteristics of tape casting ceramic slurry, green and sintered tapes were also studied.

2. Experimental

2.1. Starting materials

$Ce_{0.9}Gd_{0.1}O_{1.95}$ (GDC) powders were synthesized by the nitrate-fuel combustion method. Citric acid was used as an organic fuel and high purity (>99.9%) cerium nitrate [$Ce(NO_3)_3\cdot 6H_2O$] and gadolinium nitrate [$Gd(NO_3)_3\cdot 6H_2O$] were used as precursor reagents. The details of the method have been reported elsewhere [24]. For preparing the slurry, distilled water was used as the solvent. Poly acrylic acid (PAA) with molecular mass of 1800 g mol^{-1} was used as an electrosteric dispersant. Poly ethylene glycol (PEG) with molecular mass of 200 g mol^{-1} was used as the plasticizer. Poly vinyl alcohol (PVA) with molecular mass of 70,000–100,000 g mol^{-1} was used as the binder. Octanol was selected as defoamer and 2,4,7,9-tetramethyl-5-decyne-4,7-diol ethoxylate as surfactant. The pH value of the suspensions was adjusted by analytical grade $NH_3\cdot H_2O$ and HNO_3.

2.2. Zeta potential analysis

Zeta potential values of the GDC powder suspensions (0.01 vol.%) prepared in the absence and presence of PAA were measured with Zeta Meter 3.0 at various pH values adjusted by adding KCl (0.1 mol l^{-1}) or KOH (0.1 mol l^{-1}). The suspension was ultrasonically agitated and stirred for 20 min to achieve equilibrium between powder surface and dispersant.

2.3. Sedimentation measurements

The pH level of a suspension of 0.01 wt.% GDC with 1 wt.% PAA was adjusted by $NH_3\cdot H_2O$ and HNO_3. Then, the suspensions were poured into 50 ml graded measuring cylinders and ultrasonically agitated for 30 min. Reading of the sediment volume was recorded for 8 days.

2.4. Viscosity measurements

Viscosity of slurries with different solids loading was measured using SV-10 Sine wave vibro viscometer which employs a tuning forks vibration system and resonance feature as sensors.

2.5. Slurry preparation and tape casting

GDC powders were dispersed in distilled water containing optimum content of dispersant and defoamer with the pH adjusted within the range of 9–10 by 1 h ball milling in a poly ethylene jar with 5 and 10 mm diameter ZrO_2 balls. The plasticizer was added and the mixture was ball milled for 24 h. Then, the binder and surfactant were added to the slurry and ball milled for another 24 h to achieve good homogeneity. Before the addition of binder, the PVA was dissolved in distilled water (PVA/water ratio: 0.16) by heating the solution to 75 °C for 6 h and stirred to ensure a complete dissolution. Then, the temperature was decreased to below 35 °C while stirring.

The laboratory-scale tape casting machine with single doctor blade and moving substrate was used. A casting speed of 100 mm min^{-1} and gap height of 1 mm were set. The suspensions were cast onto a silicone-coated mylar carrier film. The details of the slurry compositions used in tape casting are given in Table 1. After tape casting, the heating bed was adjusted on 25 °C without blowing air and the tapes were left to dry for 24 h. The green tape thicknesses were in the range of 350–400 μm. The green density of the dried tapes was determined by a geometrical method. The thickness was measured using a micrometre accurate to 0.001 mm and the weight of the samples was measured using a laboratory scale accurate to 0.01 mg.

Table 1
The compositions of aqueous GDC slurries.

Slurry	Powder (wt.%)	Solvent (wt.%)	Binder[a] (wt.%)	Plasticizer (wt.%)	Dispersant (wt.%)	Surfactant (wt.%)	Defoamer (wt.%)	Viscosity (mPa s)
A	37.9	31.7	25.8	3.8	0.8	–	0.1	245
B	47.0	13.2	32	6.8	0.8	0.1	0.1	2950
C	44.6	16.2	30.1	8.1	0.8	0.1	0.1	1100

[a] The binder was prepared by dissolving PVA in distilled water (PVA/water ratio: 0.16).

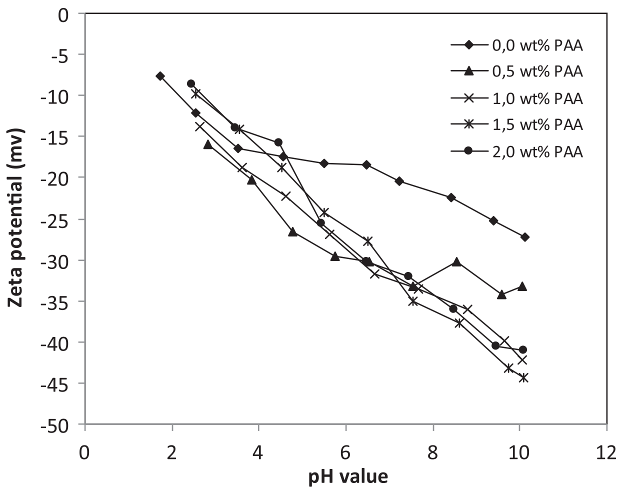

Fig. 1. Zeta potential of GDC powder as a function of pH at various amounts of dispersant.

2.6. *Thermal and microstructural analysis*

The green tape was characterized by thermogravimetric analysis (TGA) using a Netzsch-STA 449C equipped with a mass spectrometer (Netzech-QMS 403C) in He atmosphere at a heating rate of 1 and 5 °C min^{-1}. The microstructure of both green and sintered tapes was observed using a scanning electron microscopy (SEM, JEOL 6460 LV).

2.7. *Sintering*

2.7.1. *Conventional sintering*

For burning off all organic additives, the samples were heated up to 600 °C at a heating rate of 30 °C h^{-1} and held for 1 h to slowly burn off all organic additives. It was then heated at 2 °C min^{-1} and held at different temperatures and times to find out the proper condition for densification.

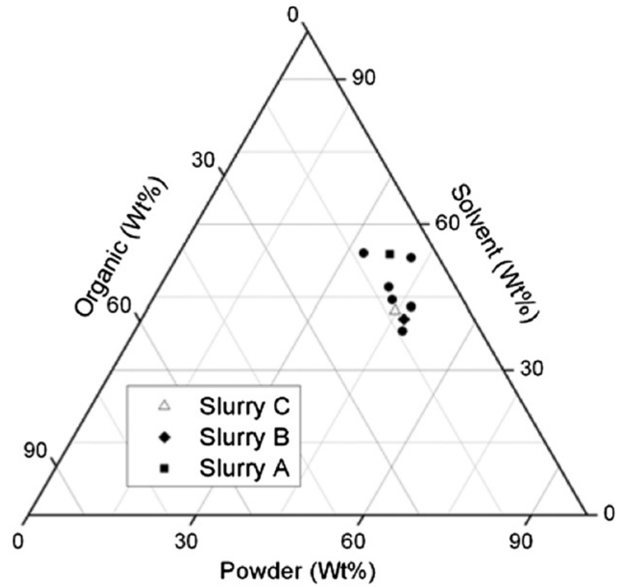

Fig. 3. Formulations of aqueous GDC slurries.

2.7.2. *Flash sintering*

Dog bone shaped specimens according to ASTM D638 Type V punched from green tapes. All organic additives were burn off with heating up to 600 °C at a heating rate of 30 °C h^{-1} and holding for 1 h and then flash sintering was performed under the application of 70 V cm^{-1} dc voltage by means of two copper electrodes at

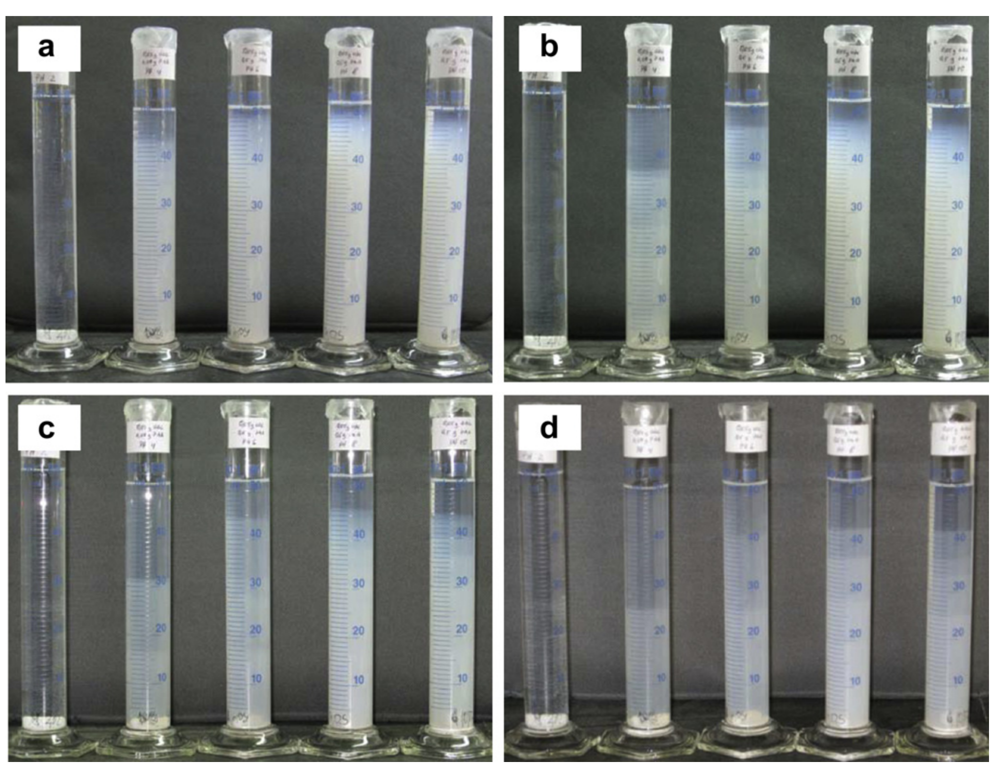

Fig. 2. Sedimentation volume of GDC vs pH value (1 wt.% PAA) (pH 2, 4, 6, 8, 10 from left to right). After (a) 2, (b) 4, (c) 6, and (d) 8 days.

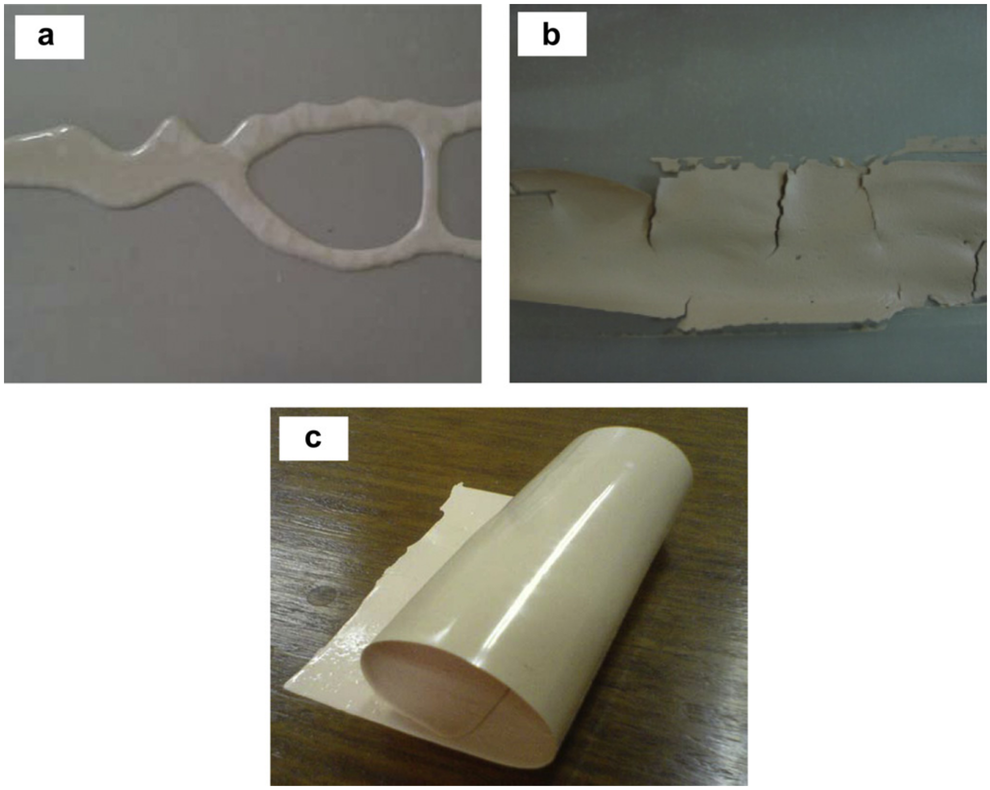

Fig. 4. Pictures of green tapes having different compositions (a) slurry A (b) slurry B and (c) slurry C.

a heating rate of 10 °C min^{-1}. The current was recorded through a Fluke 88468 digital multimeter.

3. Results and discussion

To describe the surface charge behaviour of the particles in the suspensions, zeta potential measurements were performed to identify the optimum pH value and dispersant content of GDC suspension. As shown in Fig. 1, the maximum zeta potential (absolute value) does not exceed 30 mV for the pH value range of 2–10, indicating that the electrostatic repulsion between GDC particles is insufficient for stabilizing suspension in the absence of dispersant. For the suspension containing more than 1 wt.% of PAA dispersant, the maximum zeta potential was greater than 40 mV in the pH range of 9–10. The stability of the GDC suspension with 1 wt.% of PAA was measured from the change of sediment volume as a function of pH and time. Fig. 2 shows the effect of pH on the sedimentation volume of slurries with dispersant. As it can be seen, the slurries were not well-dispersed at a low pH level around 2 and sedimentation was completed in less than 2 days. The suspension at pH 6–10 was able to sustain with a loss of approximate 25% sedimentation volume for more than 6 days. According to zeta potential and sedimentation results, 1 wt.% of PAA was used for the tape casting slurry preparation and the slurry was kept at pH 9, which is also the value reported by others [5,23].

The optimum formulation of slurry is dependent on the green tape properties such as flexibility and manageability, and also sintered tape properties such as high density. Luo et al. [5] reported an optimum formulation for 10GDC tape but they did not report about

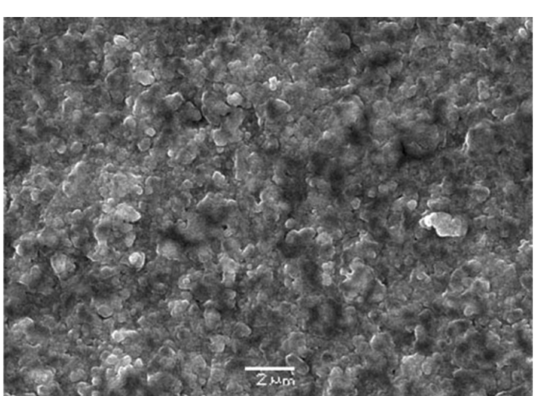

Fig. 5. SEM micrographs of GDC green tapes.

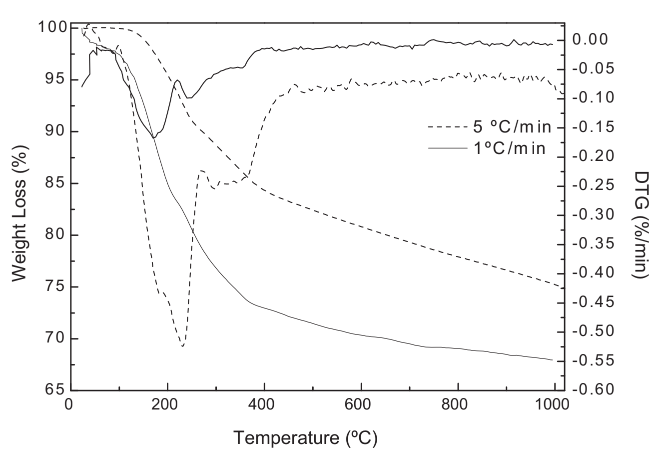

Fig. 6. TGA/DTG curves of the green tape at different heating rate.

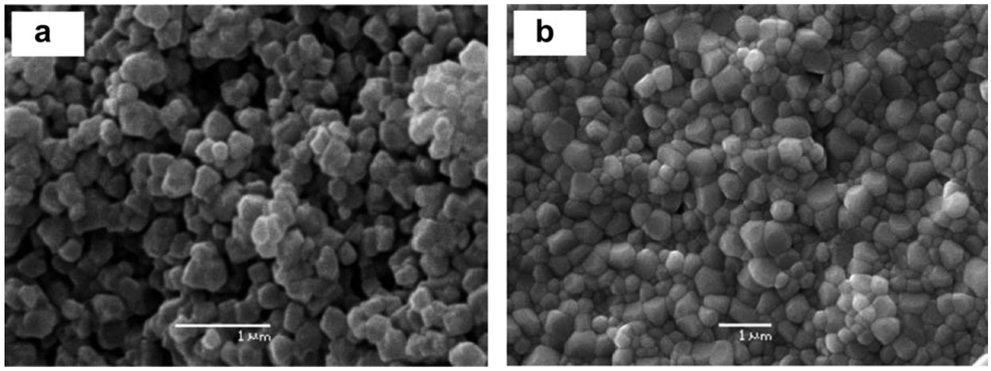

Fig. 7. SEM micrographs of GDC sintered tapes at different temperatures: (a) 1100 °C and (b) 1350 °C.

sintered tape properties or Fu et al. [23] claimed that they had achieved a highly dense and well-sintered GDC tape, but without reporting the sintering conditions. Fig. 3 shows different compositions tested in this work and Table 1 shows the viscosity and formulations of three example slurries. As can be seen in Fig. 4a, casting the slurry with the formulation A was failed because the cast tapes started to shrink and run on the carrier film. This was related to high surface tension of water and low viscosity of this slurry. To overcome this issue, surfactant was added to the slurry formulation to decrease the surface tension of water and the amount of solvent was also decreased to increase the viscosity of the slurry. Due to highly viscous slurry, tape casting has been difficult to carry out with this formulation and the cracks were formed during the drying process, which is shown in Fig. 4b. So, the slurry formulated with more solvent to achieve proper viscosity around 1 Pa s and the amount of plasticizer was increased to achieve a more flexible green tape. Fig. 4c shows the tape prepared from the slurry C, which did not show any significant defects during drying and could be bent and wrapped to exhibit its flexibility. As shown in Fig. 5, the microstructure of the top side of green tape displays very smooth surface and the average relative green density of dried tape was 45%.

Fig. 6 shows TGA/DTG analysis of the green tape at different heating rates. The weight loss of the samples showed a strong dependence on heating rate, which must be less than 1 °C min^{-1} to burn off all organic phases mainly in temperatures between 100 and 400 °C.

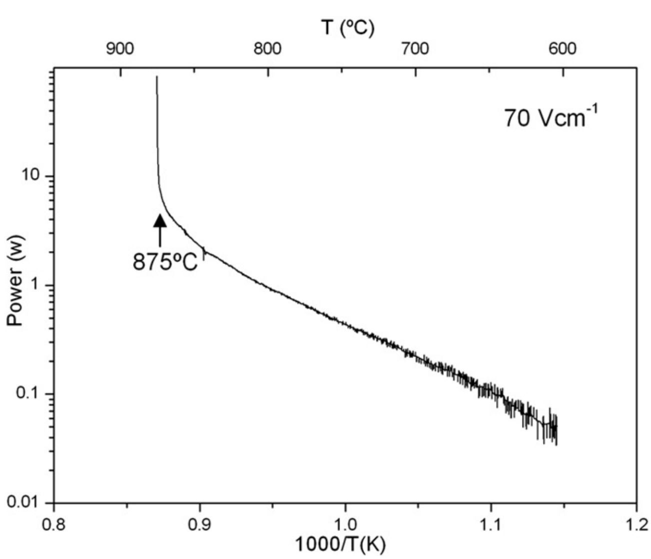

Fig. 8. Power dissipation as a function of temperature in flash sintered tape at 70 V cm^{-1}.

Microstructures of the sintered tapes at different temperatures are given in Fig. 7. GDC tapes sintered at 1100 °C have porous structures (Fig. 7a). As shown in Fig. 7b, with increasing the sintering temperature, the porosity decreased, which it is evident by observed grain growth. According to the relatively higher ionic conductivity of GDC, Hao et al. [20] have demonstrated the possibility of using flash sintering technique for sintering GDC at lower temperatures to avoid excessive grain growth. They showed the occurrence of flash sintering without any obvious grain growth at 545 °C with an applied electrical field of 70 V cm^{-1}. In this regard, we applied the same field and limited the current to a maximum of 0.5 A. Fig. 8 shows the variation of measured power as a function of temperature. As it can be seen, there is an abrupt increase in power dissipation at the temperature of 875 °C which shows the onset of flash sintering [16]. The temperature for the onset of flash sintering varies from one material to another and also depends on the contact area between the particles which changes with particle size, porosity and inhomogenity [26]. The SEM micrograph of the sample sintered with applying electric field (Fig. 9) shows a highly dense nanostructure with some pores arising from inhomogenity in the green tape. It has a smaller grain size compared with that of sintered conventionally at 1350 °C which shows not only the possibility of considerable energy and time savings but also avoiding excessive grain growth. Flash sintering phenomenon, which is simultaneous increase in electrical conductivity and mass transport kinetics, has been explained as Joule heating, but R. Raj [27] raised the doubt on this mechanism. He claimed that Frenkel pair nucleation which enhances the rate of mass transport [26,27] explained the phenomenon, although more evidence is needed to understand this phenomenon completely.

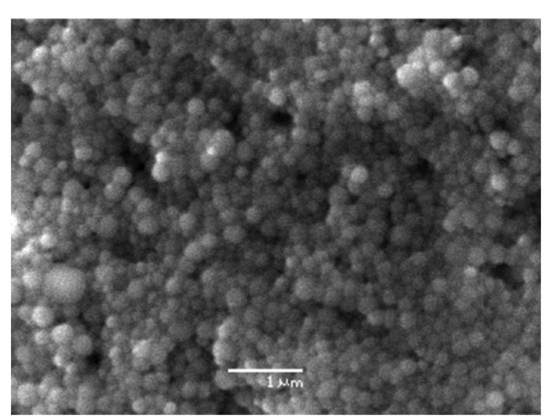

Fig. 9. SEM micrographs of GDC flash sintered tape.

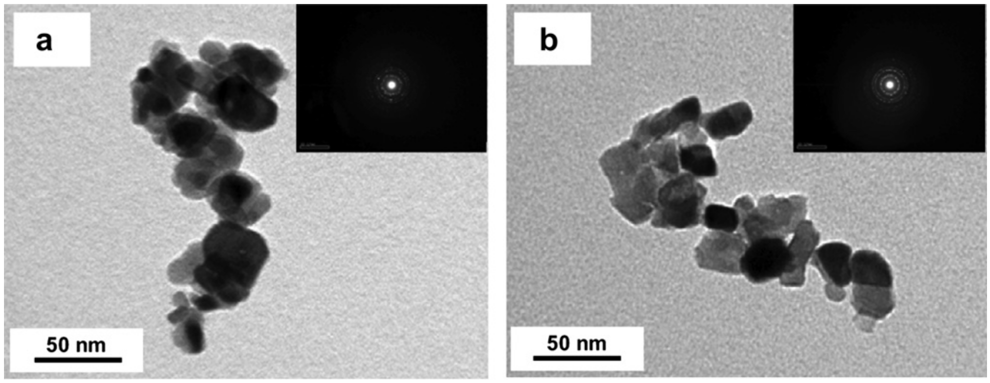

Fig. 10. TEM micrograph and selected area diffraction pattern of (a) recycled and (b) synthesized powders.

Since GDC powders are costly and scraps remain after each tape casting, it is necessary to recycle GDC powders. According to TGA/DTG analysis, we considered calcining the scraps at 400 °C for 24 h and milled for 30 min. Fig. 10 compares the microstructure and selected area diffraction patterns of recycled and synthesized powders used in this work which does not show any significant grain growth or changes during recycling.

4. Conclusions

High density nanostructured GDC electrolyte was fabricated by aqueous tape casting and novel flash sintering technique. The slurry composition was optimized by using poly acrylic acid, poly vinyl alcohol, poly ethylene glycol and double distilled water as dispersant, binder, plasticizer and solvent, respectively. The green tape displays very smooth surface and flexibility with thickness in the range of 0.35–0.4 mm and a relative green density of 45%. Microstructures of the conventionally sintered tape at 1350 °C/5 h showed fairly dense structure with unavoidable grain growth. By using flash sintering technique, the possibility of surpassing the use of costly equipment and retarding grain growth has been demonstrated.

Acknowledgements

The authors acknowledge FONDECYT, Government of Chile (Project No.: 1100349) Direction of Investigation, University of Concepcion, Chile for the support to carry out this project.

References

[1] A.U. Chavan, L.D. Jadhav, A.P. Jamale, S.P. Patil, C.H. Bhosale, S.R. Bharadwaj, P.S. Patil, Ceram. Int. 38 (2012) 3191–3196.
[2] M. Koyam, C. Wen, T. Masuyama, J. Otomo, H. Fukunaga, K. Yamada, et al., J. Electrochem Soc. 148A (2001) 795–801.
[3] B.C.H. Steele, J. Power Sources 49 (1994) 1–3.
[4] N.Q. Minh, J. Am. Ceram. Soc. 76 (1993) 563–588.
[5] L.H. Luo, A.I.Y. Tok, F.Y.C. Boey, Mater. Sci. Eng. A 429 (2006) 266–271.
[6] F. Tietz, H.-P. Buchkremer, D. Stöver, Solid State Ionics 152–153 (2002) 373–381.
[7] T. Tian, D. Jiang, J. Zhang, Q. Lin, J. Eur. Ceram. Soc. 27 (2007) 2671–2677.
[8] C. Fu, S.H. Chan, Q. Liu, X. Ge, G. Pasciak, Int. J. Hydrogen Energy 35 (2010) 301–307.
[9] M.D. Snel, G. de With, F. Snijkers, J. Luyten, A. Kodentsov, J. Eur. Ceram. Soc. 27 (2007) 27–33.
[10] D.J. Shanefield, Organic Additives and Ceramic Processing: With Applications in Powder Metallurgy, Ink, and Paint, Kluwer Academic Publishers, Boston, 1995.
[11] J.T.G. Overbeek, in: H.R. Kruyt (Ed.), Electrochemistry of the Double Layer, Colloid Science, Irreversible Systems, vol. 1, Elsevier Publishing Company, Amsterdam, 1952, pp. 115–193.
[12] J.V. Herle, T. Horita, T. Kawada, N. Sakai, H. Yokokawa, M. Dokiya, Ceram. Int. 24 (1998) 229–241.
[13] R. Orru, R. Licheri, A.M. Locci, A. Cincotti, G. Cao, Mater. Sci. Eng. R 63 (4–6) (2009) 127–287.
[14] S. Grasso, Y. Sakka, G. Maizza, Sci. Technol. Adv. Mater. 10 (2009) 053001. p. 24.
[15] R. Baraki, S. Schwarz, O. Guillon, J. Am. Ceram. Soc. 95 (1) (2012) 75–78.
[16] M. Cologna, B. Rashkova, R. Raj, J. Am. Ceram. Soc. 93 (11) (2010) 3556–3559.
[17] M. Cologna, A. Prette, R. Raj, J. Am. Ceram. Soc. 94 (2) (2011) 316–319.
[18] M. Cologna, J. Francis, R. Raj, J. Eur. Ceram. Soc. 31 (11) (2011) 2827–2837.
[19] A. Karakuscu, M. Cologna, D. Yarotski, J. Won, R. Raj, B. Uberuaga, J. Am. Ceram. Soc. (2012) 1–6.
[20] X. Hao, Y. Liu, Z. Wang, J. Qiao, K. Sun, J. Power Sources 210 (2012) 86–91.
[21] L.P. Meier, L. Urech, L.J. Gauckler, J. Eur. Ceram. Soc. 24 (2004) 3753–3758.
[22] T. Klemensø, M. Menon, S. Ramousse, Ceram. Int. 36 (2010) 773–780.
[23] Y. Fu, Y. Liu, S. Hu, Ceram. Int. 35 (2009) 3153–3159.
[24] R.V. Mangalaraja, S. Ananthakumar, U. Kasimayan, M. Romel, Jiménez, Marta Lòpez, P. Carlos Camurri, Mater. Sci. Eng. A 517 (2009) 91–96.
[25] R.V. Mangalaraja, S. Ananthakumar, Anke Schachtsiek, Marta López, Carlos P. Camurri, Ricardo E. Avilad, Mater. Sci. Eng. A 527 (2010) 3645–3650.
[26] J. Francis, M. Cologna, R. Raj, J. Eur. Ceram. Soc. 32 (2012) 3129–3136.
[27] R. Raj, J. Eur. Ceram. Soc. 32 (2012) 2293–2301.